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# Titanium Dioxide as Energy Storage Material: A Review on Recent Advancement

*Tarun Parangi and Manish Kumar Mishra*

## Abstract

With the increased attention on sustainable energy, a novel interest has been generated towards construction of energy storage materials and energy conversion devices at minimum environmental impact. Apart from the various potential applications of titanium dioxide ( $\text{TiO}_2$ ), a variety of  $\text{TiO}_2$  nanostructure (nanoparticles, nanorods, nanoneedles, nanowires, and nanotubes) are being studied as a promising materials in durable active battery materials. The specific features such as high safety, low cost, thermal and chemical stability, and moderate capacity of  $\text{TiO}_2$  nanomaterial made itself as a most interesting candidate for fulfilling the current demand and understanding the related challenges towards the preparation of effective energy storage system. Many more synthetic approaches have been adapted to design different nanostructures for improving the electronic conductivity of  $\text{TiO}_2$  by combining with other materials such as carbonaceous materials, conducting polymers, metal oxides etc. The combination can be done through incorporating and doping methods to synthesize  $\text{TiO}_2$ -based anodic materials having more open channels and active sites for lithium and/or sodium ion transportation. The present chapter contained a broad literature and discussion on the synthetic approaches for  $\text{TiO}_2$ -based anodic materials for enhancing the lithium ion batteries (LIBs) and sodium ion batteries (SIBs) performance. Based on lithium storage mechanism and role of anodic material, we could conclude on future exploitation development of titania and titania based materials as energy storage materials.

**Keywords:** Titanium Dioxide, Nanomaterial, Nanostructure, Lithium Ion Battery

## 1. Introduction

Nowadays, investigation in the field of energy storage and conversion devices with different functionalities is emerging subject for many research investigators [1–3]. Since last two decades, the regular efforts are being implemented towards the development of nanostructured as electrochemical storage materials convenient to access both surface and bulk properties and hence a superior storage and conversion performance. In this view, nanostructured materials are of great interest due to easy availability for modification into degree of crystallinity, phase, particle size, morphology and porosity which are prior characteristics.

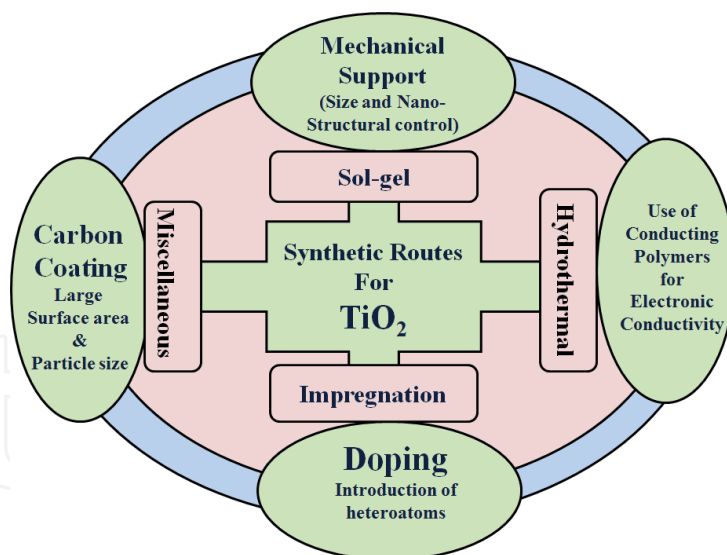
As a talk of nanomaterials and nanotechnology, titania ( $\text{TiO}_2$ ) and titania-based materials always been studied first.  $\text{TiO}_2$  nanoparticles (NPs) are being widely

investigated over the past few decades due to their unique characteristics such as non-toxicity, abundance, thermal and chemical stability, and easy availability. Many more research and progress reports on  $\text{TiO}_2$  have shown a great potential in various important applications such as photocatalysis, biomedical, environmental remediation and many more. Beyond these applications,  $\text{TiO}_2$  and  $\text{TiO}_2$ -based nanomaterials also offers novel materials to overcome the energy and environment related challenges. Different  $\text{TiO}_2$  nanostructures with high surface area, large pore volumes, tunable pore structures and nano-confined effects have been synthesized and used in various fields with excellent performances [4]. In the past, many comprehensive reviews have been documented on synthesis, properties and applications of  $\text{TiO}_2$  and  $\text{TiO}_2$ -based nanomaterials.

In view of energy storage technologies, recently, lithium-ion batteries (LIBs) are found to be emerging technologies for imperative electric grid applications such as mobile electronics, electric vehicles and renewable energy systems operating on alternating energy sources like wind, tidal, solar and other clean energy sources [5, 6]. The performance of these technologies in terms of capacity, recyclability and rate capability are much more dependent on the characteristics of the active anode and cathode materials. The performance can be improved through fundamental modification with particular strategy with such factors like the power capacity, long term durability and most prior its cost. In this view of direction, finding of energy storage materials with high efficiency and low cost is thrust challenge for the materials scientists. As we talked about various important characteristics of  $\text{TiO}_2$ , it could be suitable candidate due to its versatile functionalities. The present chapter covering literature on the recent progress of applications of  $\text{TiO}_2$  and  $\text{TiO}_2$  based materials as energy storage technologies and discussion on the efforts that have been made so far.

Theoretically, the anode part has a crucial role in LIBs and thus, the direction towards development of anode materials is one of the most essential factors which could define the performance of the device [7]. As an ideal anode material, it should possess high specific surface area allowing better insertion for mobile ions (lithium ions for LIBs); large pore size, low volume change and low internal resistance for speedy charging and discharging; low intercalation potential for mobile ions; and operating at moderate condition with economical and environmental benefits.

Among available various suitable anode materials, transition metal oxides in which  $\text{TiO}_2$  is following the characteristics of an ideal anode material that makes  $\text{TiO}_2$  itself as most promising anode material for LIBs. Apart from these benefits and utilities of  $\text{TiO}_2$ , some drawbacks still exist like low capacity and poor rate capability [4, 7]. Thus,  $\text{TiO}_2$  suffering from poor ionic/electronic conductivity that limits the lithium storage rate. However, the transport of electrons and  $\text{Li}^+$  ions can be promoted by engineering of their physicochemical and morphological characteristics as presented in **Figure 1**. In this view, many more researches and efforts have been made to overcome the said disadvantages by designing and adopting different synthetic strategies to obtain various forms of  $\text{TiO}_2$  such as zero-dimensional (0D) nanospheres, one dimensional (1D) nanostructures, two-dimensional (2D) nanoarchitectures and three-dimensional (3D) hierarchical nanostructures with different electronic structures. These nanostructures are showing the advantages of providing high contact surface area with the electrolyte as well as short diffusion pathways for electrons and mobile ions such as  $\text{Li}^+$  and  $\text{Na}^+$ . In addition, the adoption like doping of different heteroatoms into  $\text{TiO}_2$  lattice which could alter the chemical and physical surface of  $\text{TiO}_2$  would open more channels and active sites for transportation of mobile ions due to which electrical conductivity can be increased [7].



**Figure 1.**  
*Synthetic approaches for TiO<sub>2</sub> based anode materials.*

## 2. Synthesis approaches and nanostructural forms

Generally, synthetic strategy is crucial tool to design the structural characteristics due to which materials functionality can be optimized for better performance. Interestingly, TiO<sub>2</sub> can be synthesized in such manner to have different structural forms and hence, versatile functionalities. To summarize recent structural development of titania, this chapter started with a brief introduction on the synthesis and structural characteristics of TiO<sub>2</sub> which has great impact on the performances.

In search of synthesis routes for fabrication of TiO<sub>2</sub>-based materials, sol-gel, hydrothermal/solvothermal and impregnation methods of preparation are well recognized. Sol-gel synthesis is mode of preparation offering optimization of various experimental parameters at moderate conditions and allows designing material structure with customized properties. Generally, sol-gel route is widely used to synthesize hybrid and composite types materials by using aqueous and non-aqueous mode in suitable solvent media. In this finding, performance based composite-TiO<sub>2</sub> materials to be used as energy storage materials have been synthesized by sol-gel route. Hydrothermal process consist of treatment of bulk TiO<sub>2</sub> with alkaline solution at high temperature and pressure using Teflon reactor or autoclave instrument. The reaction conditions of pressure and temperature yields selective product which decide the morphology and functionalities of the materials. By use of these useful synthetic techniques, various kind of TiO<sub>2</sub>-based materials can be prepared as anode materials in LIBs or/and SIBs applications.

### 2.1 Carbon coating approach

This approach has received much attention providing superior electrical conductivity, large surface-to-volume ratio, and excellent mechanical and chemical stabilities. In this view many more research works have been done successfully. Kim *et al.* [8] have synthesized anatase TiO<sub>2</sub> nanorods by a hydrothermal method followed by carbon coating in order to improve the electric conductivity through carbonization of pitch used as a carbon source at 700°C for 2 h in Ar flow. The obtained nanorods have been tested for their electrochemical activity in a sodium cell. As results, this anatase TiO<sub>2</sub> nanorod material demonstrates an acceptable cycling performance and a rate capability compared to 1D anatase nanowire TiO<sub>2</sub> and nanowire TiO<sub>2</sub> bulk.



In Na cell tests, carbon coated anatase nanorod attain a capacity of  $\sim 193 \text{ mA}\cdot\text{h}\cdot\text{g}^{-1}$  on the first charge. The presence of carbon on nanorods surface helps to improve the electrode stable performance with high-rate capability up to the current of 100 C-rate. From the mechanism, the chemical characteristic of anatase nanorod  $\text{TiO}_2$  supports a  $\text{Ti}^{4+}/^{3+}$  redox reaction based on  $\text{Na}^+$  intercalation during electrochemical reaction in the Na cell. This study shows carbon-coated anatase nanorod  $\text{TiO}_2$  material would be a promising anodic material in rechargeable sodium batteries [8]. Zou *et al.* [9] have developed a facile aqueous sol-gel process to synthesize a porous anatase  $\text{TiO}_2$  by coatings on carbon nanotubes (CNTs). In this controlled hydrolysis process,  $\text{TiO}_2$  NPs form a thin layer of 20 nm uniformly and continuously covering the surface of CNTs to form an amorphous film without loss of  $\text{TiO}_2$  NPs. The capacitive performance of the  $\text{TiO}_2/\text{CNT}$  hybrid electrodes has been evaluated by cyclic voltammetry (CV) and galvanostatic charge-discharge technique using Land battery testing system in the cutoff voltage window of 1–3 V at a scan rate of  $50 \text{ mV}\cdot\text{S}^{-1}$  in 0.5 M  $\text{H}_2\text{SO}_4$  electrolyte. From this measurement, an ideal rectangular shape was observed in the CV curve of the  $\text{TiO}_2/\text{CNT}$  composite indicating the ideal electrochemical double-layer capacitive behavior of the electrode. The observed good performance and cyclic durability of  $\text{TiO}_2/\text{CNT}$  composite is attributed to the nanometer sized particles facilitate faster charge-discharge rates. In addition, the supported CNTs also has been served as an electron transferring medium and its uniformly coating provides an excellent connection between them to facilitates fast electron exchange, and hence the enhanced electronic conductivity. The calculated average energy density and power density of the  $\text{TiO}_2/\text{CNT}$  composite are found to be  $\sim 10.6 \text{ W}\cdot\text{h}\cdot\text{kg}^{-1}$  and  $0.954 \text{ kW}\cdot\text{kg}^{-1}$  at  $5 \text{ mV}\cdot\text{s}^{-1}$  respectively. The porosity of the composite is beneficial for improving contact with electrolyte and reducing the  $\text{Li}^+$  ions during application as anode for LIBs. The obtained finding of high specific capacitance and high cycle durability values for the  $\text{TiO}_2/\text{CNT}$  composite makes itself as a promising candidate for supercapacitor application. [9]

Zhang *et al.* [10] have adopted a combined sol-gel and hydrothermal routes for the preparation of multi-walled carbon nanotubes (MWCNT) core and mesoporous  $\text{TiO}_2$  sheath by using hexadecylamine as a structure directing agent. The prepared  $\text{CNT}@$ mesoporous  $\text{TiO}_2$  hybrid nanocables exhibited with well-crystallized quality, porous feature and large surface area, favoring its electrochemical performance. The introduced CNTs enhance the electronic conductivity. Lithium ion ( $\text{Li}^+$ ) insertion/extraction behavior has been studied to identify the capacity contribution from CNTs in the voltage range of 1–3 V. A stable specific capacity of the  $\text{CNT}@$ mesoporous  $\text{TiO}_2$  hybrid nanocables could be recovered its initial value after the 30th cycle tested under different current densities even up to current of 10C indicating the high reversibility of lithium ion insertion/extraction in this electrode. The conducted study shows a stable cycling performance with reversible capacities of  $\sim 183 \text{ mA}\cdot\text{h}\cdot\text{g}^{-1}$  at current rate of 1C and  $\sim 112 \text{ mA}\cdot\text{h}\cdot\text{g}^{-1}$  at current rate of 10C retained after 70 cycles. These results suggesting the uses the  $\text{CNT}@$ mesoporous  $\text{TiO}_2$  hybrid nanocables in various fields like photocatalysis and dye-sensitized solar cells. Trang *et al.* [11] have synthesized a stable hybrid mesoporous material through comprised of mesoporous  $\text{TiO}_2$  spheres and MWCNTs via a combined sol-gel and solvothermal method. The obtained  $\text{TiO}_2/\text{MWCNT}$  composite has been used as an anode material with a high specific capacity and superior rate capability. In this concept, the MWCNTs served as conducting channels connecting each of the mesoporous  $\text{TiO}_2$  spheres in order to form an interconnected network to transport electrons efficiently and therefore the conductivity and stability of the composite can enhance the storage capacity of the lithium ion devices. The composite exhibited with very good LIBs performance with a discharge capacity of  $\sim 316 \text{ mA}\cdot\text{h}\cdot\text{g}^{-1}$  with good reversibility and stability after 100 cycles. The mesoporous nature of

the composite offered more open channels for  $\text{Li}^+$  ion extraction. The thin walls of the mesoporous  $\text{TiO}_2$  reduced the Li ion diffusion length in the solid phase while the pores allowed  $\text{Li}^+$  ions to flow smoothly. The mesoporous features allow to  $\text{TiO}_2/\text{MWCNT}$  composite to be used as anode materials significantly for LIBs [11]. Wang *et al.* [12] have implemented a green one-pot hydrothermal process to synthesize hybrid mesoporous  $\text{CNT}@\text{TiO}_2\text{-C}$  nanocable using anatase  $\text{TiO}_2$ , CNT and glucose (as carbon source) as for structure directing agent. The prepared hybrid  $\text{CNT}@\text{TiO}_2\text{-C}$  resulted with one-dimensional nanostructure of the CNT with the diameters ranging from 20 to 30 nm. The use of CNT provides high electronic conductivity, high mechanical strength and large-scale availability. The  $\text{CNT}@\text{TiO}_2\text{-C}$  nanocable has been used as anode material for LIBs. The CV analysis curve shows an ideal rectangular shape in the range of 1.0–1.7 V, that are characteristic of charging/discharging of supercapacitance contributed from the anatase  $\text{TiO}_2$  and carbon. Two peaks at approximately 1.73 V (cathodic) and 1.98 V (anodic) observed are associated with  $\text{Li}^+$  insertion/extraction into/from the anatase  $\text{TiO}_2$ . These peaks show almost no change in amplitude and voltage positions during the subsequent several cycles, indicating good stability and high reversibility of the electrochemical reaction. The charge–discharge profiles of the nanocable shows a sloped charge–discharge voltage profiles at different rates which is attributed to the decreased crystallite size of  $\text{TiO}_2$  and the porous nanostructure of the hybrid material. The observed performance shows an excellent high-rate long-term cycling stability with a high charge capacity of  $\sim 187 \text{ mA}\cdot\text{h}\cdot\text{g}^{-1}$  after 2000 cycles at current of 5 C and  $\sim 122 \text{ mA}\cdot\text{h}\cdot\text{g}^{-1}$  after 2000 cycles at current of 50 C. The study reveals about high specific capacity, superior rate capability, and excellent long term cycling stability  $\text{CNT}@\text{TiO}_2\text{-C}$  nanocable as anode material for LIBs in half cell. [12].

MWCNT array has been grown on a  $\text{SiO}_2$  precursor via combustion chemical vapor deposition (CCVD) method and then prepared  $\text{TiO}_2$  precursor have been deposited onto MWCNT/ $\text{SiO}_2$ . The characterization results for the obtained material confirmed positive preliminary data about the capacitance and energy density. The analyzed data proved to be potential as an improvement over comparable electrochemical capacitance device. The present idea of hybridization can be used in current electrochemical theory to create an energy storage device that is both efficient and inexpensive [13]. He *et al.* [14] have synthesized hierarchical rod-in-tube structured  $\text{TiO}_2$  with a uniform conductive carbon layer using solvothermal method. With help of modification routes via solvent selection, the morphologies of the prepared  $\text{TiO}_2/\text{C}$  composite can be modified to design various forms like nanoparticles, microrods and microtubes. These modified composites have been tested for their specific capacities for sodium storage capability by using the Na half-cell with a counter electrode consisting of a sodium metal disk, an electrolyte of  $\text{NaClO}_4$  dissolved in a 1: 1:1 volumetric mixture of dimethyl carbonate, ethylene carbonate (EC), and ethyl methyl carbonate with 5% fluoroethylene carbonate additive and a working electrode of prepared rod-in-tube  $\text{TiO}_2/\text{C}$  composite. As a result, a rod-in-tube  $\text{TiO}_2/\text{C}$  found to be highest electronic conductivity, specific surface area and more porosity compared to other composite materials. These characteristics features with stable crystal texture of a rod-in-tube  $\text{TiO}_2/\text{C}$  composite shows high discharge capacity values of  $\sim 277 \text{ mA}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$  at  $50 \text{ mA}\cdot\text{g}^{-1}$  and  $\sim 153 \text{ mA}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$  at  $5000 \text{ mA}\cdot\text{g}^{-1}$  which are retained over 14000 cycles. The improved electronic conductivity was resulting from the homogeneous carbon layers derived from the carbonization of absorbed solvent which also affects to the electron transfer process, but also suppress the clustering and volume change of  $\text{TiO}_2$  nanocrystals during the cycling process. The present synthetic modification routes can lead to a design more advanced materials with better storage performance for SIBs [14].

Liu *et al.* [15] have reported scalable synthesis strategy to fabricate a nano-composite of anatase TiO<sub>2</sub> NPs anchored on CNTs using ammonia water assisted hydrolysis and *in situ* crystal transformation under calcination in Ar at 500°C. In the fabricated nanostructured TiO<sub>2</sub>/CNT, interweaved CNTs has been served as a highway for electrons to facilitate the charge transfer process. The nano-sized TiO<sub>2</sub> found to be useful to improve its contact area with electrolyte and reduced the Li<sup>+</sup> ions diffusion path due to which Li<sup>+</sup> transportation could be accelerated. As results of CV analysis and galvanostatic discharge/charge measurement, the prepared composite exhibited with superior rate capability and cycling stability values of ~92 mA·h·g<sup>-1</sup> and retained at a current density of 10 A·g<sup>-1</sup> at current of 60C. The observed results for this hybrid TiO<sub>2</sub>/CNT are comparable higher than that of commercial TiO<sub>2</sub> with 80% anatase and 20% rutile phases. The adopted synthetic strategy is eco-friendly, economical and highly scalable for the preparation of anatase-TiO<sub>2</sub>/CNTs nanocomposite that holds potential as a superior anode material for high-power LIBs [15]. Cho *et al.* [16] have synthesized phase-pure anatase TiO<sub>2</sub> nanofibers with fiber-in-tube and filled structures by electro-spinning process using tetra-*n*-butyl titanate-polyvinylpyrrolidone (TBT-PVP) composite nanofibers under oxygen and air atmospheres respectively. An intermediate product of carbon free TiO<sub>2</sub> nanofibers with a fiber-in-tube with a core-shell nanostructure was obtained through burning of TiO<sub>2</sub>/C composite under oxygen atmosphere during a short time. The repeated combustion and contraction of the TiO<sub>2</sub>/C composite core part by burning of the carbon layer lead to formation of the nanofiber with a yolk-shell structure of TiO<sub>2</sub>/C@void@TiO<sub>2</sub>. These prepared materials have been used as anode materials for LIBs properties using 2032-type coin cells in which electrodes have been prepared using a slurry consisting of 70 wt% active anode material, 20 wt% carbon black as a conductive material, and 10 wt% binder composed of sodium carboxymethyl cellulose (CMC) on a copper foil. As results of electrochemical impedance spectroscopy (EIS) measurements, anatase TiO<sub>2</sub> nanofibers with a fiber-in tube structure exhibited with a superior Li-ion storage capacity (~231 mA·h·g<sup>-1</sup>) compared to TiO<sub>2</sub> nanofibers with a filled structure (~134 mA·h·g<sup>-1</sup>) and commercial TiO<sub>2</sub> nanopowder (~223 mA·h·g<sup>-1</sup>). The TiO<sub>2</sub> nanofibers with the fiber-in-tube structure shows a low charge transfer resistance and structural stability during cycling and rate performances compared to other materials studied in this study [16].

Liao *et al.* [17] have synthesized self-supported, three-dimensional (3D) single-crystalline nanowire array electrodes by using simple hydrothermal process. In this study TiO<sub>2</sub>, TiO<sub>2</sub>-C and TiO<sub>2</sub>-C/SnO<sub>2</sub> have been produced on flexible Ti foil and used as anode materials for electrochemical performance in LIBs using 2032-type coin cells with two electrodes assembled in an Ar filled dry glove box with the prepared materials as working electrodes and Li metal as the counter electrode. The results showing that TiO<sub>2</sub>-Sn/C core-shell nanowires exhibit an enhanced electrochemical cycling and rate capability compared to the pure TiO<sub>2</sub> and TiO<sub>2</sub>-SnO composite nanowires. A single-crystalline TiO<sub>2</sub>-Sn/C core shell nanowire electrodes exhibits a good cycling performance with a discharge capacity higher than ~160 mA·h·g<sup>-1</sup> and a capacity retention rate of ~84% even after 100 cycles at a current rate of 10 C. These results could be attributed to such factors like high theoretical capacity of Sn, long cycling stability due to TiO<sub>2</sub> nanowire with self-supported array structures, the space between nanowires is large enough to accommodate the volume changes of Sn during charge/discharge, which can also help to maintain the integrity of the anode during cycling, the carbon shell can suppress cracking and improve the conductivity of the electrode and each nanowire anchored directly to the current collector can help to fast charge transport. With similar intention of successful preparation of carbon containing TiO<sub>2</sub> hybrid composite materials, a



single crystalline TiO<sub>2</sub>, TiO<sub>2</sub>-C and TiO<sub>2</sub>-C/MnO<sub>2</sub> core-double-shell nanowire arrays on flexible Ti foil through a layer-by-layer deposition technique has been reported [18]. In this synthetic approach, MnO<sub>2</sub> NPs produced on a TiO<sub>2</sub>-C nanowire surface by combination of in situ chemical redox reaction between carbon and KMnO<sub>4</sub> using a facile soaking process. The electrochemical characteristics of the prepared materials have been investigated for use in LIBs. The study shows that, TiO<sub>2</sub>-C/MnO<sub>2</sub> core double-shell nanowires performed well with enhanced electrochemical cycling and rate properties compared to that of the TiO<sub>2</sub> and TiO<sub>2</sub>-C nanowires. For TiO<sub>2</sub>-C/MnO<sub>2</sub>, a high charge/discharge capacity and stable rate performance of ~332 mA·h·g<sup>-1</sup> at current rate of 2C. The observed improved electrochemical performance is attributed to the stable structure of the TiO<sub>2</sub> nanowire core, high conductivity of the carbon layer, higher active surface area, and high theoretical capacity of MnO<sub>2</sub> NPs. This study reveals about the adopted layer-by-layer synthetic method proven to be useful technique for preparing unique single crystalline TiO<sub>2</sub>-C/MnO<sub>2</sub> nanowire arrays those would be promising anode material for advanced carbon black and binder free LIBs applications. The above two studies [17, 18] can open new ideas for the preparation of self-supported TiO<sub>2</sub>/carbon composite based core-shell nanostructures for having better electrochemical performance in the field of LIBs applications.

In addition, graphene oxide (GO) can be considered as another conducting carbon source which has a good ability to form a composite with TiO<sub>2</sub> by using various synthetic techniques. Many more significant research works are in progress to find feasibility for GO through combined with TiO<sub>2</sub> in the field of energy storage materials. Farooq *et al.* [19] have reported a scalable process for *in situ* synthesis of TiO<sub>2</sub> NPs on reduced GO nanosheets by a microwave hydrothermal process to prepared homogenously dispersed and high performance based TiO<sub>2</sub>-rGO nanocomposite as anode materials for LIBs. For electrochemical measurement, slurry of the prepared materials was formed and coated onto copper foil, and lithium foil and polypropylene (PP) membrane were used as the counter electrode and a separator respectively. As an electrolyte liquid, 1 M lithium hexafluorophosphate (LiPF<sub>6</sub>) dissolved in ethylene carbonate (EC) and dimethyl carbonate (DMC) (1: 1 in vol %) have been used. The results of electrochemical impedance spectroscopy reveal that high rate capability and cycle stability have been achieved with developed TiO<sub>2</sub>-rGO electrodes. The well-integrated rGO nano-filler enhanced the electronic conductivity enabling the increased rate capability of the electrodes. The present study demonstrates a potential use of the prepared TiO<sub>2</sub>-rGO nanocomposite as a viable anode material in advanced Li-ion battery applications which require high power. In the similar way of success, Yue *et al.* [20] have used a simple hydrothermal process to synthesize three dimensional (3D) mesoporous TiO<sub>2</sub> nanocubes grown on RGO nanosheets without use of any surfactants and high temperature of calcination. The prepared TiO<sub>2</sub>/RGO composite formed with mesoporous structure contained both rutile and anatase crystalline phases. TiO<sub>2</sub>/RGO composite has been exhibited with a very good lithium storage performance as anode materials for LIBs with high specific capacity value of ~180 mA·h·g<sup>-1</sup> at current rate of 1.2C after 300 cycles. The observed performances is attributed to the relatively large surface area and stable mesoporous structure. The performed above two studies [19, 20] reveal the importance of the synthesis strategy about the formation of desired nanostructure with exploring experimental condition that would give a better performance.

Gao *et al.* [21] have reported sol-gel synthesis of anode materials consisting of mixed (DND) and TiO<sub>2</sub> hollow nanospheres for improving the specific capacity of LIBs. The obtained hybrid material (DND/TiO<sub>2</sub>) exhibits high lithium adsorption capacity, large specific surface area and chemical inertness probably due to beneficial characteristics of detonation nanodiamond and porous structure of TiO<sub>2</sub>. The



electrochemical measurements has been performed using two electrodes of CR2025 button cells in which working electrode made of 80% active material (DND/TiO<sub>2</sub>), 10% carbon black and 10% polyvinylidene fluoride (PVDF) and 1 M LiPF<sub>6</sub> used as electrolyte. From the capacity performance results, this active material found to be a good anodic material for LIBs with reversible capacity value of ~348 mA·h·g<sup>-1</sup> at current of 0.5 C after 100 cycles, high rate performance and long-term cyclic stability value of ~246 mA·h·g<sup>-1</sup> at current of 5 C after 800 cycles. The observed performance of this material is found to be superior to that of traditional TiO<sub>2</sub> anode. This study can lead to develop and design anodic materials consisting nanodiamond mixed with other suitable material to have improved and stable performance based LIBs in practical application fields [21].

## 2.2 Doping approach

This has been well established method for the introduction of impurities into the semiconductor crystal to intentionally change its conductivity due to deficiency or excess of electrons [22]. Tanaka *et al.* [23] have synthesized mesoporous spherical anatase TiO<sub>2</sub> by one-pot solvothermal process using carboxylic acids as organic additives in supercritical methanol medium. The obtained TiO<sub>2</sub> nanostructure can be considered to be roundly integrated metal oxides evaluated as anode materials for Li<sup>+</sup>-ion and Na<sup>+</sup>-ion batteries. The authors also have developed Nb-doping mesoporous TiO<sub>2</sub> with an aim to improve electrochemical performance for LIBs. The electrochemical measurements of Li-insertion (charge) and extraction (discharge) has been carried out using 2032-type coin half cells that consisted of Li metal sheets and glass fiber as separator. 1 M bis(trifluoromethanesulfonyl)amide (LiTFSA) dissolved in propylene carbonate has been used as electrolyte. Nb-doped spherical mesoporous TiO<sub>2</sub> exhibited with larger surface area than that of commercial TiO<sub>2</sub>. As results of Galvanostatic charge–discharge analysis, the excellent electrochemical performance observed for Nb-doped TiO<sub>2</sub> with the discharge (Li-extraction) capacity of ~147 mA·h·g<sup>-1</sup> at the 1000th cycle at a high current rate of 10C. The observed performance can be compared to that Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> or a Li<sup>+</sup>-ion battery negative electrode. The similar performance observed for Nb-doped for Na-batteries with the discharge (Na-extraction) capacity of ~128 mA·h·g<sup>-1</sup> upto 1000 cycles. This performance is attributed to Nb doping into TiO<sub>2</sub> providing large reaction area and it also improved electronic conductivity and broadening the ion-diffusion path in TiO<sub>2</sub> [23]. Synthesis optimization, structural analysis, characterization of the dielectric properties and energy storage density of rutile TiO<sub>2</sub> ceramics co-doped with niobium (Nb<sup>5+</sup>) and erbium (Er<sup>3+</sup>) have been investigated [24]. The material (Er<sub>0.5</sub>Nb<sub>0.5</sub>)<sub>x</sub>Ti<sub>1-x</sub>O<sub>2</sub> obtained with dense microstructure and smaller grain size distribution giving rise to its high permittivity performance in the subsequent dielectric properties. The observed both intrinsic and extrinsic defect states could be expected to be responsible for the observed high-performance colossal permittivity. As results, the co-doping of Er<sup>3+</sup> and Nb<sup>5+</sup> have produced enhanced dielectric properties, where Nb<sup>5+</sup> ions contribute to a large dielectric permittivity and Er<sup>3+</sup> decreased dielectric loss. The conducted study suggesting that the prepared co-doped TiO<sub>2</sub> ceramics are favorable for solid-state capacitor and high-energy-density storage applications [24].

## 2.3 By using conducting polymer

This approach also has gained much attention because of high electrical conductivities and good redox properties of such conducting polymeric materials. Polyoxometalates (POMs), a well-known class of transition metal oxide

nanoclusters with interesting structures and diverse properties can give a nano-composite of TiO<sub>2</sub>. In this view, Qu *et al.* [25] have reported synthesis of hybrid bifunctional nanocomposite film of TiO<sub>2</sub> nanowires and POMs, using combination of hydrothermal and layer-by-layer self assembly methods. The prepared nano-composite film has been tested as anode material for electrochemical performance in which three-electrode system used consisting the as-prepared film served as the working electrodes; Pt plate/Pt wire and Ag/AgCl played the roles of counter electrode and reference electrode, and 1 M LiClO<sub>4</sub>/propylene carbonate used as electrolyte. The originated electrochemical properties are due to the unique 3D structures of TiO<sub>2</sub> nanowires which provide a larger electrolyte contact area and shorter ion diffusion pathway available for the redox reactions. As results of electrochemical performance, this composite film shows a high coloration efficiency ( $\sim 150 \text{ cm}^2 \cdot \text{C}^{-1}$  at 600 nm) and cyclic stability with its volumetric capacitance about  $\sim 172 \text{ F} \cdot \text{cm}^{-3}$  with working voltage window of  $\sim 1.77 \text{ V}$ , and maintained after 1000 cycles at  $0.18 \text{ mA} \cdot \text{cm}^{-2}$ . The favorable adsorption of ions and the transport of charges with a very low resistance represents to this composite film as a suitable anodic material for electrochromic and energy storage applications [25].

## 2.4 Combination with other semiconductors

Ngaotrakanwivat *et al.* [26] have investigated energy storage capacity of nanocrystalline TiO<sub>2</sub> mixed with V<sub>2</sub>O<sub>5</sub> with different compositions using sol-gel synthesis process at different calcination temperatures. The prepared TiO<sub>2</sub>-V<sub>2</sub>O<sub>5</sub> composite film has been used as a working electrode immersed in a three-electrode electrochemical cell with Ag/AgCl electrode and Pt-wire as a reference electrode and counter electrode, respectively. The obtained TiO<sub>2</sub>-V<sub>2</sub>O<sub>5</sub> composite with Ti:V (TiO<sub>2</sub>:V<sub>2</sub>O<sub>5</sub>) molar ratio of 1:0.11 calcined at 550°C shows higher energy storage capacities compared to other paired samples and pure WO<sub>3</sub>. The performance could be due to the availability of high surface area ( $\sim 1.75 \text{ cm}^2$ ) and hence the enhanced ion mobility and intercalation rate.

## 2.5 Impregnation method

Deka *et al.* [27] have developed a form-stable composite of 1-tetradecanoic acid (TDA) and TiO<sub>2</sub> powder using a facile impregnation method. The long-term chemical and thermal reliability have been investigated by applying 1000 melting-freezing cycles to the composite sample under set temperature range between 20°C and 90°C. The conducted study has demonstrated about a good chemical compatibility and crystalline structure which would be useful for thermal management of electronic devices, automotive components, photovoltaic thermal hybrid designs, solar air/water heating systems, etc.

## 2.6 Miscellaneous

Hierarchical TiO<sub>2</sub> sphere composed of ultrathin nanotubes consist of both anatase and rutile phases have been synthesized from a low-temperature hydrothermal reaction and calcination process [28]. The obtained hierarchical TiO<sub>2</sub> ( $\sim 78\%$  anatase and  $\sim 21\%$  rutile phases) used as-prepared electrode mixed with acetylene black and binder of sodium-CMC in a weight ratio of 7:2:1 using distilled water as solvent. The solution was placed on a copper foil as the current collector and the electrode dried in a vacuum oven at 100°C for 24 h. From this electrochemical tests, prepared material showing the superior performance in Li-storage with a specific capacity of  $\sim 167 \text{ mA} \cdot \text{h} \cdot \text{g}^{-1}$  at  $1 \text{ A} \cdot \text{g}^{-1}$  current of 6C and maintained  $\sim 187 \text{ mA} \cdot \text{h} \cdot \text{g}^{-1}$

at rate of  $10 \text{ A}\cdot\text{g}^{-1}$  at current rate of 60C. The capacity retention rate was  $\sim 97\%$  at  $1 \text{ A}\cdot\text{g}^{-1}$  and  $\sim 92\%$  at  $2 \text{ A}\cdot\text{g}^{-1}$  after 500 cycles. The present performance is attributed to the presence of both phases of  $\text{TiO}_2$  due to which the synergistic effect has been originated between the defective anatase and rutile renders the shared conduction of electrons through the anatase and  $\text{Li}^+$  ions via the rutile at high current rates. In addition, pathway for electron and  $\text{Li}^+$  ion conduction was found to be shortened. Also, the interfacial boundaries between the two phases can contribute to extra capacitance at high rates by forming a  $\text{Li}^+/\text{e}^-$  double layer. Overall, the synergy between the anatase and rutile phases, and interfacial storage are revealed to be beneficial for the high-kinetic reaction in lithium-ion batteries [28]. Anatase phase mesoporous  $\text{TiO}_2$  has been synthesized using the urea assisted hydrothermal process and used for high power performance for LIBs applications [29]. The material obtained as mono-phasic  $\text{TiO}_2$  sub-microspheres of uniform particle size with I41/ and space group. From the rate capability behavior, material has a specific charge capacity of  $\sim 162 \text{ mA}\cdot\text{h}\cdot\text{g}^{-1}$  at current rate of 0.5 C and slightly reduced to 160, 154 and  $147 \text{ mA}\cdot\text{h}\cdot\text{g}^{-1}$  at 1, 5 and 10C-rates, respectively. The obtained good performance due to the large surface area ( $\sim 116 \text{ m}^2\cdot\text{g}^{-1}$ ) introduced by the highly porous (pore size of  $\sim 7 \text{ nm}$ ) nano-structured building blocks of each anatase  $\text{TiO}_2$  sub-microspheres resulting to make favorable and short diffusion pathway for ionic and electronic diffusion. The near zero strain behavior of this anatase phase mesoporous  $\text{TiO}_2$  makes it a suitable anode material for high power lithium applications.

Serrapede *et al.* [30] have compared and quantified the charging mechanisms of defective  $\text{TiO}_2$  with respect to stoichiometric anatase. The porous  $\text{TiO}_2$  samples have been synthesized by simple thermal oxidation of titanium foil in a 111 volume hydrogen peroxide solution (30% (w/w) in  $\text{H}_2\text{O}$ ) at low temperature. Two different thermal treatments have been applied to form a defective  $\text{TiO}_2$  by annealing the as-grown material in Ar atmosphere at  $150^\circ\text{C}$  and a stoichiometric  $\text{TiO}_2$  by air annealing at  $450^\circ\text{C}$ . These  $\text{TiO}_2$ -based electrodes have been used for energy-storage applications by using three electrode cell in de-aerated 1 M  $\text{LiPF}_6$  in EC:DMC with a Li foil and a Li ring as counter and reference electrodes, respectively. As results, the defective  $\text{TiO}_2$  exhibited a higher Li molar fraction with respect to the crystalline one, with a common diffusion-controlled charging-discharging mechanism, initiated by  $\text{Li}^+$  ions. A rapid extraction, with respect to  $\text{Li}^+$  ion-insertion was observed in both samples. With the theoretical capacity of stoichiometric  $\text{TiO}_2$ , it was found to be stable for 200 cycles while the defective material exhibited with a lower capacity and it maintained stable even after 1550 cycles. Moretti *et al.* [31] have performed electrochemical test for the nanocrystalline anatase  $\text{TiO}_2$  electrodes synthesized by using sodium-CMC binder, alone and in combination with styrene butadiene rubber (SBR) via aqueous process. The electrochemical behavior of these electrodes has been compared with those of electrodes manufactured using traditional polyvinylidene difluoride (PVDF) and its copolymer with hexafluoropropylene (PVDF-HFP) in N-methyl-2-pyrrolidone solution. In case of CMC-based electrodes, a spontaneous reaction of CMC towards the electrolyte probably due to the presence of hydroxide groups at the surface leading to the formation of a surface film, whose presence appears to be beneficial with respect to the first cycle behavior. The study demonstrated that  $\text{TiO}_2$  electrodes consist of CMC or without CMC/SBR mixture as binder material exhibit an improved electrochemical performance (energy density of  $\sim >120 \text{ mW}\cdot\text{h}\cdot\text{g}^{-1}$ ) compared to those based fluorinated binders. The adopted aqueous process has been facilitated as environmental friendly and cost-effective fluorine free lithium-ion electrode preparation process.

$\text{TiO}_2$  bulk NPs have been synthesized using modified hydrothermal process under aqueous medium [32]. Their behavior as an intercalation host for  $\text{Li}^+$  ions has been explored by performing an electrochemical test in which the active material

Sr. No.	TiO <sub>2</sub> based anode materials and method of synthesis	LIBs or SIBs performance	Ref.
<b>A Carbon Coating Approach</b>			
1	Anatase TiO <sub>2</sub> nanorods synthesized by a hydrothermal method followed by carbon coating	Capacity of ~193 mA·h·g <sup>-1</sup> on the first charge in a sodium cell	[8]
2	Porous anatase TiO <sub>2</sub> synthesized by aqueous sol-gel process followed by coatings on carbon nanotubes (CNTs)	Reversible capacity as high as ~200 mA·h·g <sup>-1</sup> at a current density of 0.1 A·g <sup>-1</sup> for LIBs	[9]
3	CNT@mesoporous TiO <sub>2</sub> hybrid nanocables prepared by a combined sol-gel and hydrothermal route by using hexadecylamine as a structure directing agent	Discharge capacity as high as ~183 mA·h·g <sup>-1</sup> at current of 1 C for LIBs	[10]
4	TiO <sub>2</sub> /MWCNT composite prepared using via a combined sol-gel and solvothermal method	Discharge capacity as high as ~316 mA·h·g <sup>-1</sup> with good reversibility and stability after 100 cycles	[11]
5	Hybrid mesoporous CNT@TiO <sub>2</sub> -C nanocable using anatase TiO <sub>2</sub> , CNT and glucose (as carbon source) as for structure directing agent.	charge capacity of ~187 mA·h·g <sup>-1</sup> after 2000 cycles at current of 5 C and ~ 122 mA·h·g <sup>-1</sup> after 2000 cycles at current of 50 C for LIBs	[12]
6	Prepared TiO <sub>2</sub> precursor deposited onto MWCNT/SiO <sub>2</sub> using combustion chemical vapor deposition (CCVD) process	Performance that is significantly better and more applicable than current electrochemical capacitors for LIBs	[13]
7	Hierarchical rod-in-tube structure TiO <sub>2</sub> with a uniform conductive carbon layer using solvothermal method	Discharge capacity values of ~277 mA·h <sup>-1</sup> ·g <sup>-1</sup> at 50 mA·g <sup>-1</sup> and ~ 153 at 5000 mA·g <sup>-1</sup> and retained over 14000 cycles	[14]
8	Anatase TiO <sub>2</sub> NPs anchored on CNTs using ammonia water assisted hydrolysis and <i>in situ</i> crystal transformation under calcination in Ar at 500°C	Cycling stability values of ~92 mA·h·g <sup>-1</sup> remained at a current density of 10 A·g <sup>-1</sup> at current of 60 C in LIBs	[15]
9	Phase-pure anatase TiO <sub>2</sub> nanofibers with fiber-in-tube and filled structures by electro-spinning process using tetra- <i>n</i> -butyl titanate-polyvinylpyrrolidone	Li-ion storage capacity (~231 mA·h·g <sup>-1</sup> )	[16]
10	Self-supported, three-dimensional single-crystalline nanowire array electrodes by using simple hydrothermal process: TiO <sub>2</sub> , TiO <sub>2</sub> -C and TiO <sub>2</sub> -C/SnO <sub>2</sub> have been produced on flexible Ti foil	Discharge capacity higher than ~160 mA·h·g <sup>-1</sup> and a capacity retention rate of ~84% even after 100 cycles at a current rate of 10 C	[17]
11	A single crystalline TiO <sub>2</sub> , TiO <sub>2</sub> -C and TiO <sub>2</sub> -C/MnO <sub>2</sub> core-double-shell nanowire arrays on flexible Ti foil through a layer-by-layer deposition technique	Performance of ~332 mA·h·g <sup>-1</sup> at current of 2 C in LIBs	[18]
12	TiO <sub>2</sub> NPs on reduced GO nanosheets by a microwave hydrothermal process	Discharge capacity of ca. 100 mA·h·g <sup>-1</sup> with >99% coulombic efficiency at C-rates of up to 20 C in LIBs	[19]
13	Hydrothermal process to synthesize 3D mesoporous TiO <sub>2</sub> nanocubes grown on RGO nanosheets without use of any surfactants and high temperature of calcination	LIBs with high specific capacity value of ~180 mA·h·g <sup>-1</sup> at current of 1.2 C after 300 cycles	[20]



Sr. No.	TiO <sub>2</sub> based anode materials and method of synthesis	LIBs or SIBs performance	Ref.
14	Mixed detonation nanodiamond (DND) and TiO <sub>2</sub> hollow nanospheres synthesized by sol-gel route	LIBs with reversible capacity value of ~348 mA·h·g <sup>-1</sup> at current of 0.5 C after 100 cycles	[21]
<b>B Doping Approach</b>			
15	Nb-doping mesoporous TiO <sub>2</sub> by one-pot solvothermal process using carboxylic acids as organic additives in supercritical methanol medium.	Li-extraction capacity of ~147 mA·h·g <sup>-1</sup> at the 1000th cycle at a high current rate of 10 C Na-extraction capacity of ~128 mA·h·g <sup>-1</sup> upto 1000 cycles	[23]
16	TiO <sub>2</sub> ceramics co-doped with niobium (Nb <sup>5+</sup> ) and erbium (Er <sup>3+</sup> )	Better dielectric properties than the singly-doped ones	[24]
<b>C By using conducting polymer</b>			
17	Hybrid bifunctional nanocomposite film based on TiO <sub>2</sub> nanowires and Polyoxometalates (POMs) using combination of hydrothermal and layer-by-layer self assembly methods	Coloration efficiency (~150 cm <sup>2</sup> ·C <sup>-1</sup> at 600 nm) and cyclic stability with its volumetric capacitance about ~172 F·cm <sup>-3</sup> with working voltage window of ~1.77 V, and maintained after 1000 cycles at 0.18 mA·cm <sup>-2</sup>	[25]
<b>D Combination with other semiconductors</b>			
18	Nanocrystalline TiO <sub>2</sub> mixed with V <sub>2</sub> O <sub>5</sub> with different compositions using sol-gel synthesis process at different calcination temperatures	Energy storage ability: Initial charging rate of ~3700 C·mol <sup>-1</sup> ·h <sup>-1</sup>	[26]
<b>E Impregnation Method</b>			
19	Form-stable composite of 1-tetradecanoic acid (TDA) and TiO <sub>2</sub> powder using a facile impregnation method	Superior thermal stability with latent heat storage capacity of ~97 J·g <sup>-1</sup>	[27]
20	Hierarchical TiO <sub>2</sub> sphere composed of ultrathin nanotubes having mixed anatase and rutile phases synthesized from a low-temperature hydrothermal reaction and calcination	Specific capacity of ~167 mA·h·g <sup>-1</sup> at 1 A·g <sup>-1</sup> current of 6 C and maintained ~187 mA·h·g <sup>-1</sup> at 10 A·g <sup>-1</sup> at current of 60 C	[28]
21	Anatase phase mesoporous TiO <sub>2</sub> synthesized using the urea assisted hydrothermal process	Specific charge capacity of ~162 mA·h·g <sup>-1</sup> at current rate of 0.5 C and slightly reduced to 160, 154 and 147 mA·h·g <sup>-1</sup> at 1, 5 and 10 C-rates, respectively	[29]
22	Porous TiO <sub>2</sub> samples have been synthesized by simple thermal oxidation of titanium foil	LIBs Stable for 200 cycles	[30]
23	Nanocrystalline anatase TiO <sub>2</sub> electrodes synthesized by using sodium carboxymethyl cellulose (CMC) binder, and in combination with styrene butadiene rubber (SBR) via aqueous process	Energy density of ~ >120 mW·h·g <sup>-1</sup>	[31]
24	TiO <sub>2</sub> bulk NPs synthesized using modified hydrothermal process under aqueous medium	High capacity than other titanate materials at rated above 1000 mA·g <sup>-1</sup> .	[32]

**Table 1.** Synthesis methods and electrochemical performances for TiO<sub>2</sub>-based materials.

(TiO<sub>2</sub>) mixed with poly(vinylidene fluoride) and Super P carbon in the weight ratio of 70:20:10, then introduced into an electrochemical cell along with a lithium metal counter/reference electrode and liquid electrolyte. The mixture was cast onto copper foil from acetone using the Doctor-Blade technique. From this test, gravimetric capacity for the TiO<sub>2</sub> bulk NPs at all rates up to 18000 mA·g<sup>-1</sup> was found to be identical to the 6 nm anatase particles which have a much higher proportion of carbon content. In comparison from nanowires to nanotubes and nanoparticles, the amount of Li and hence charge that can be stored, even at low rates, increased with reduced dimensions. The volumetric capacity of composite electrodes with nanoparticulate TiO<sub>2</sub> bulk was found to be notably high than other titanate materials at rated above 1000 mA·g<sup>-1</sup>.

**Table 1** summarizes discussed synthetic modification processes for TiO<sub>2</sub>-based materials to be used as anode materials for LIBs or SIBs.

### 3. Role of anode in LIBs: the aging mechanism

The anodic materials is operating in organic electrolyte such as LiPF<sub>6</sub> with co-solvents like ethylene carbonate (EC), dimethyl carbonate (DMC), diethyl carbonate (DEC), methyl ethyl carbonate (EMC) [33, 34]. Generally, the most important part of the LIBs cell is the anode/electrolyte interface because of high reactivity of the organic electrolyte with any type of electrode material and lithium ions for LIBs. Due to the interaction occurring between the composite anode and the electrolyte solution would form organic species on the anode surface that can be recognized as solid electrolyte inter-phase (SEI). The produced organic species can undergo reduction with CO<sub>2</sub> and traces of H<sub>2</sub>O in the electrolyte to form lithium carbonate which further react with used organic solvents to form transesterification products. On other hand, anion contaminates, such as F<sup>-</sup> from HF and PF<sub>5</sub>, readily react with lithium to form insoluble reaction products which are non-uniform, electronically insulating, and unstable on the surface of the anodic material. At higher battery potentials, during the intercalation of lithium ions into the anode lattice structure, within the reactions continue, the consumption of lithium ions with co-solvents can precipitate and grow on the anode surface. This process consequently results in the formation of a protective, ionically conductive but electrically insulating passive layer on the surface of the anode during the first charge cycle, the so-called SEI. This SEI creates resistance to lithium ion flow, which results in a rise in the charge transfer resistance and the impedance of the anode. This increase follows charge rate, cycle number, temperature, and surface area/particle size of anodic material. The stable growth of SEI may leads to the loss of active lithium and further decomposition of the electrolyte. This phenomenon is the main degradation mechanism in fully charged batteries at storage conditions [33, 34].

Furthermore, interactions of the anode with the cathode should be included because of the dissolution of the cathode electrode metal from the lattice into the electrolyte solution may occur when batteries stored at voltages greater than ~3.6 V [34]. This may cause deposition of cation contaminates which are incorporated into the SEI layer. This kind of reactions can damage SEI and a short circuit may be generated, which then can lead to thermal runaway and battery failure.

Fracture and decrepitating of the electrodes are critical challenges existing in lithium-ion batteries as a result of lithium diffusion during the charging and discharging operations. A large volume change on the order of a few to several hundred percent can be observed due to lithium ions intercalate and de-intercalate. Thus, diffusion-induced stresses (DISs) generate the nucleation and growth of

cracks/damages, leading to mechanical degradation of the active electrode materials. Therefore, for nanoscale electrode structures, surface energies and surface stresses can be predictable to have an important impact on the mechanical properties of the electrode materials.

### **3.1 Effect of particle size, active surface area and porosity of the anode material**

Generally, small particles contain short diffusion paths between the anodic particles, which make easy and fast charge and discharge rate the. Similarly, large surface area of the anodic material are prone to higher internal heat generation and lithium ion are consumed during the exothermic reaction at high temperatures ( $> 60^{\circ}\text{C}$ ) compared to larger particles size, this leads to an enhancement in the irreversible capacity of the anodic material. There is no a direct connection between the porosity of the anode and the reversible capacity of the anode. At high temperature ( $> 120^{\circ}\text{C}$ ), heat generation from a denser electrode material produces gaseous species through thermal decomposition of the SEI layer. This reveals about the importance of the thermal stability of an anodic material. Overall, the anode of the lithium ion battery undergoes several degradation mechanisms during aging. Ion ( $\text{Li}^+$ ) plating is one aging mechanism which ends the life of a battery more rapidly due to the formation and growth of lithium dendrites. These kinds of degradation mechanisms rarely affect the crystal structure of the anode electrode.

In comparison with Li-ion insertion mechanism where  $\text{Li}_3\text{OCl}$  forms as an intermediate, the presence of  $\text{Na}_3\text{OCl}$  is not observed as an intermediate product after the first conversion due to it is metastable and its limited lifetime [35].

## **4. Conclusions**

In conclusions, the huge amounts of efforts are in progress towards the synthesis, characterization and application of  $\text{TiO}_2$  based anode materials in the fields of LIBs. Development can be seen with an aim to gain the superior electrochemical performance and promote the practical utilities of the synthesized  $\text{TiO}_2$ -based functionalized materials. The synthesis strategies have played a crucial role to establish a material composition with a desired nanostructure and appropriate morphologies including particle size/shape and surface area by adopting different modification methods as discussed in the chapter. The effective synthesis condition can easily provides material informations with unique characteristics and hence high lithium or sodium storage capacity and cyclic stability which are depend on ion flux at the electrode/electrolyte interface, internal resistance and diffusion path.

The energy storage capacity strongly influenced by materials structure and morphologies, thus various structural forms should be explored to enhance the electrochemical performance of modified  $\text{TiO}_2$  materials. The chapter providing a bunch of literature reports on how synthetic process can alter the nanostructure that facilitates the electrochemical performance at minimum cost and good durability. The formation of one dimensional (1D), two dimensional (2D) and three dimensional (3D) hierarchical nanostructures have been found to be much stable materials for electrochemical performance. The doping approaches also can open more windows to modified  $\text{TiO}_2$  matrices and therefore different structural forms. The uniformly carbon coating also making a huge impact on formation of  $\text{TiO}_2$  based modified materials with good surface area and electronic conductivity favoring good energy storage performances. The use of various carbon sources like CNTs, MWCNT and graphene oxide have formed the homogenously dispersed nanocomposites showing a stable cyclic performance for LIBs.

Overall, progressive research works have been well established for TiO<sub>2</sub> to be used as anode materials in the field of energy storage. Although, still challenges are there to improve the Li ion storage performance like low coulombic efficiency, low volumetric energy density etc. To solve the fundamental issues, more development towards material surface alteration or coating to reduce unwanted side reactions and designing hierarchical structural materials by adopting different experimental conditions.

In addition, on other hand, sodium ion battery (SIBs) getting more attention which has to be used as thrust area of research. The prepared materials should be performed for LIBs and SIBs as well.

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## Conflict of interest

The authors declare no conflicts of interest.

## Acronyms and abbreviations

NPs	Nanoparticles
LIBs	Lithium Ion Batteries
SIBs	Sodium Ion Batteries
0D	Zero-dimensional
1D	One-dimensional
2D	Two-dimensional
3D	Three-dimensional
Ar	Argon
RGO & rGO	Reduced Graphene Oxide
CNTs	Carbon Nanotubes
MWCNT	Multi-walled Carbon Nanotubes
CCVD	Combustion Chemical Vapor Deposition
TBT	Tetra- <i>n</i> -butyl titanate
PVP	Polyvinylpyrrolidone
EIS	Electrochemical Impedance Spectroscopy
DND	Detonation Nanodiamond
POMs	Polyoxometalates
PVDF	Polyvinylidene Difluoride
HFP	Hexafluoropropylene
SBR	Styrene Butadiene Rubber
CMC	Carboxymethyl Cellulose
LiTFSA	bis(trifluoromethanesulfonyl)amide.
PP	Polypropylene
EC	Ethylene Carbonate
DMC	Dimethyl Carbonate
DEC	Diethyl carbonate
EMC	Methyl Ethyl Carbonate



SEI                    Solid Electrolyte Inter-phase  
DIS                    Diffusion-Induced Stresses

## **Appendices and nomenclature for scientific units**

nm	Nanometer
cm	centimeter
°C	Degree Celsius
C	Coulomb
h	hour
mA	mili Ampere
g	gram
F	Farad
V	Volt
W	Watt
s	Second

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### **Author details**

Tarun Parangi\* and Manish Kumar Mishra  
Department of Chemistry, Sardar Patel University,  
Vallabh Vidyanagar, Gujarat, India

\*Address all correspondence to: juvenile34@gmail.com

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